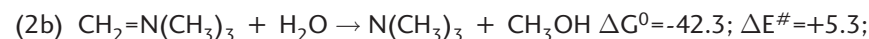
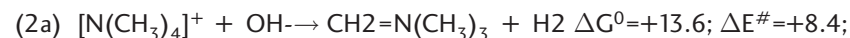
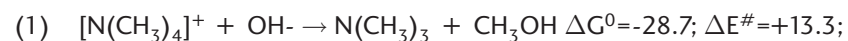


Molecular Modeling of Alkaline Fuel Cell Membranes

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Alkaline membrane fuel cells (AMFC) have the potential to replace the acidic proton-exchange membrane fuel cells (PEMFC) for use in vehicular and portable applications [1]. Alkaline media allow for the use of non-precious electrode catalysts made from inexpensive metals such as Fe/Co/Ni and thus avoid the use of rare precious metals such as Pt and Ru [2]. In AMFCs, electrolyte membranes that contain tetraalkylammonium head groups such as $[\text{N}(\text{CH}_3)_4]^+$ are used. Unfortunately, hydroxide ions tend to react chemically with these head groups and form neutral species. This reaction between cation and hydroxide serves as the ultimate limit for membrane lifetime, and limits the applications where this technology can be used. We have used B3LYP/6-311++g(2d,p) level theory, polarizable continuum models, and reaction-path-finding algorithms [3] to study such reactions. We have also performed molecular dynamics simulations to probe the microstructure of alkaline membranes (Fig. 1).

Degradation of tetramethylammonium, $[\text{N}(\text{CH}_3)_4]^+$, is found to occur through two pathways as shown below (energies in kcal/mol). The reactant and product structures are also depicted in Fig. 2.



The small barrier (8.4 kcal/mol) calculated for ylide formation (Reaction 2a) suggests that rapid scrambling of methyl protons and aqueous protons should be observable in H-D isotope exchange experiments. Mass spectrometry of the gases [4] released in the thermal decomposition of $[\text{N}(\text{CH}_3)_4]^+[\text{OD}]^- \cdot 5(\text{D}_2\text{O})$ does indeed reveal rapid scrambling of the protons of $[\text{N}(\text{CH}_3)_4]^+$ with the $[\text{OD}]^-$ and D_2O .

Transition state structures for different cations are shown in Fig. 3. In an alkaline membrane operating under fuel cell conditions, half of the volume is the non-aqueous phase (the polymer backbone) with the balance as the aqueous phase (water, cationic head groups, and OH^-) as shown in Fig. 1. To probe the effect of water and solvation on reactivity we repeated the ΔG^0 and ΔE^\ddagger evaluations with different dielectric constants in the PCM model and found that reactions are faster at lower water content (Fig. 4).

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- [2] J.S. Spendlow, A. Wieckowski, *Phys. Chem. Chem. Phys.*, **9**, 2654 (2007).
- [3] S. Chempath, C++ Source Code for Implementing the Growing String Method and Finding Transition States (<http://zeolites.cqe.northwestern.edu/shaji/growstring.html>).
- [4] B.R. Einsla et al., *ECS Transactions*, **11**, 1173 (2007).

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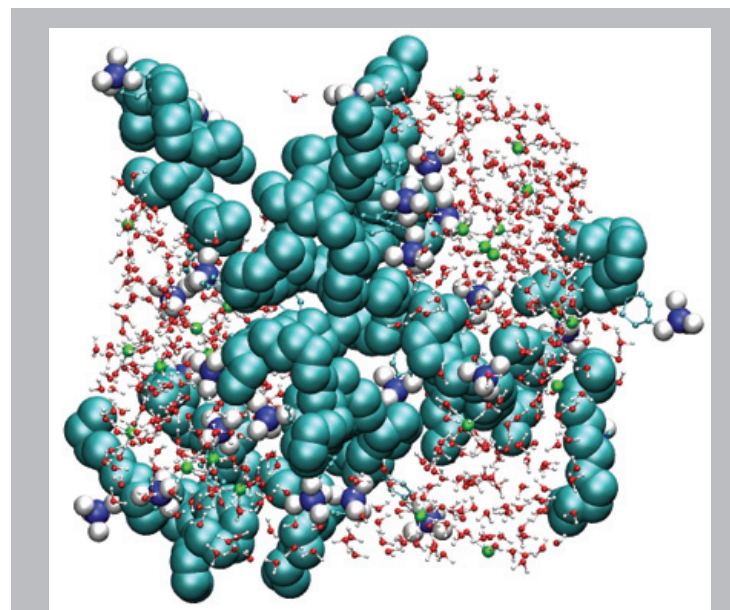


Fig. 1. Microstructure of alkaline membrane (blue spheres: fluorocarbon backbone, red: water).

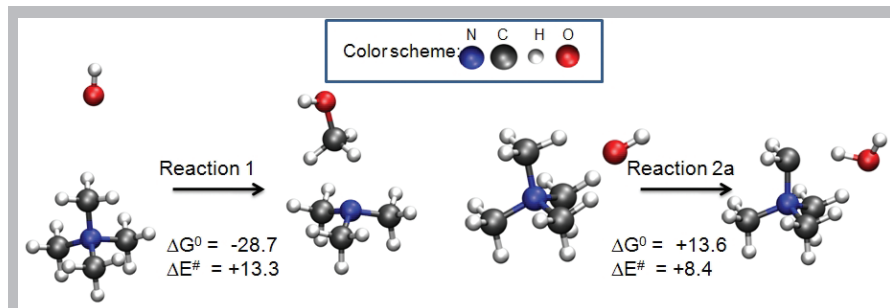


Fig. 2. Two mechanisms for $[N(CH_3)_4]^+$ degradation.

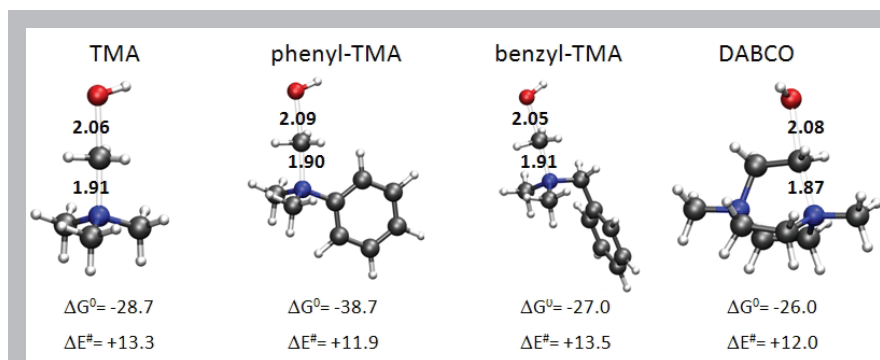


Fig. 3. Transition state structures for the S_N2 attack on tetramethylammonium (TMA), phenyltrimethylammonium (phenyl-TMA), benzyltrimethylammonium (benzyl-TMA), and diazabicyclooctane (DABCO).

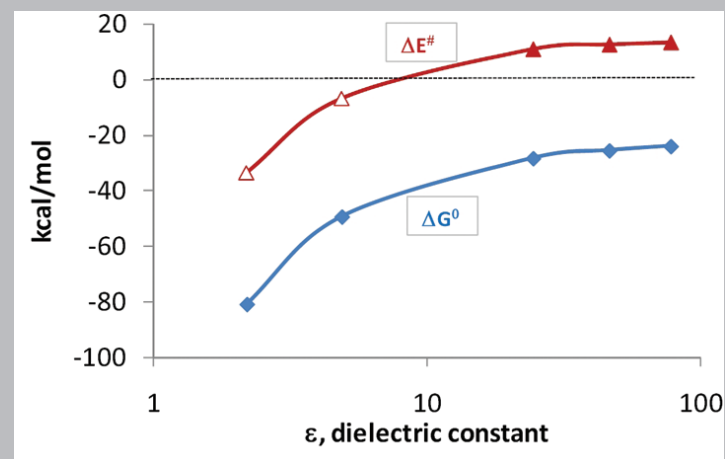


Fig. 4. The barrier (ΔE^\ddagger) for the degradation of $[N(CH_3)_4]^+$ becomes small at low water content (at low ϵ).